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THE INFLUENCE OF ATMOSPHERES OF NITROGEN AND HYDROGEN ON THE ARC SPECTRA OF IRON, ZINC, MAGNESIUM, AND TIN, COMPARED WITH THE INFLUENCE OF AN ATMOSPHERE OF AMMONIA.

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Presented by C. R. Cross, May 14, 1902. Received October 8, 1902.

It has been frequently assumed that chemical reactions in the electric arc have a considerable influence on the character of its radiations.* It seems not unreasonable to expect that the oxidation of the electrodes at high temperature in air would tend to increase the intensity over that obtained when the arc is operated in nitrogen alone. This presumed higher temperature might be sufficient to produce atomic vibrations entirely distinct from the vibrations at a lower temperature. If the atmosphere does have any such influence, the effect might be apparent in the spectrum of the arc.

In the case of a hydrogen atmosphere † the most marked effects on the arc spectra of iron, zinc, magnesium, and tin have been found to be a general diminution of intensity and a change of relative intensity among the lines. The lines relatively enhanced by hydrogen are spark lines.

Liveing and Dewar ‡ have noted the effect of atmospheres of hydrogen and nitrogen on a number of lines in the magnesium arc and spark, and of these and other atmospheres on the cyanogen § bands in the carbon arc, but as far as I am aware no extensive study has been made of the influence of nitrogen and ammonia on the arc spectrum of metals. From a study of the effects of hydrogen and nitrogen on certain spark lines of magnesium, Liveing and Dewar[*] were led to remark that "it is possible that the atmosphere may, besides the resistance it offers to the discharge, in some degree affect the vibrations of the metallic particles." This conclusion in regard to the spark seems to have been borne out with reference to the arc by the results obtained with a hydrogen[†] atmosphere.

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* Liveing and Dewar, Proc. Roy. Soc., **30**, 161 (1880); **32**, 192 (1881); O. H. Basquin, Astroph. Jour., **14**, 11-12 (1901); A. S. King, Astroph. Jour., **14**, 329-330 (1901).

† H. Crew, Astroph. Jour., **12**, 167 (1900); Liveing and Dewar, Proc. Roy. Soc., **32**, 192, 402-403.

‡ Proc. Roy. Soc., **32**, 189-203 (1881).

§ Ibid., **30**, 152-162.

Nitrogen resembling hydrogen in its inability to combine directly with metals, it seemed reasonable to expect that it would have a very similar effect on the iron, zinc, and tin arcs. As magnesium[‡] combines directly with nitrogen a different effect might be expected in the magnesium arc.

Method and Apparatus.[§]

In order to eliminate the effect of gases other than the one whose effect was being studied, the enclosed rotating metallic arc,[||] with "chemically pure" zinc, magnesium, and tin electrodes, was used. The iron used, however, was "commercial." The speed of the rotating electrode was approximately eleven hundred revolutions per minute. Excepting in two instances noted later, the arc was operated by a 104 volt alternating circuit.

The spectrum was photographed with a Rowland ten-foot concave grating, four exposures being made on each plate, as shown in the diagram.

Long exposure, arc in air.
Long exposure, arc in gas.
Short exposure, arc in gas.
Short exposure, arc in air.

Near the top of the plate was photographed the spectrum of the arc in air; just below this, was photographed the same arc operated in an atmosphere of the gas being studied; below this, again, was made a short exposure with the arc in the same gas; and at the bottom, a short exposure with the arc in air. The exposures were so timed as to make the intensities of the two inner photographs intermediate between the intensities of the two outer ones. By comparison one can readily determine from such a plate whether any change in intensity is due to length of exposure or to change of atmosphere. This plan of making four exposures on each plate has some additional advantages: (1) it affords a test of uniformity of results; (2) the two short exposures allow an easier comparison of lines so strong as to be ordinarily over-exposed; (3) the second exposure in the gas being made immediately after the first, and without opening the "hood" of the arc, a photograph is obtained of the spectrum of the arc in its final atmosphere; that is, in an atmosphere which includes the gaseous products of the arc, if there be any.

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[*] Proc. Roy. Soc., **32**, 203 (1881).

[†] Astroph. Jour., **12**, 167–175 (1900).

[‡] Liveing and Dewar, Proc. Roy. Soc., **32**, 161.

[§] The funds to meet the expense of this experiment were kindly appropriated by the Committee in charge of the Rumford Fund of the American Academy of Arts and Sciences.

[||] Crew and Tatnall, Phil. Mag., **38**, 379–386 (1894).

The effect of hydrogen was taken from the results published by Professor Crew * and from the original plates obtained by him. These negatives were made under the same conditions as here described, except in a different atmosphere and with a direct current. The change from a direct to an alternating current, however, produces no effect on the spectrum. In the case of the tin arc less dust is produced when a direct current is used, and I have therefore employed such a current in photographing the spectrum of tin in ammonia.

The hydrogen atmosphere was obtained by the electrolysis of acidulated water. The ammonia used was taken from a drum of compressed ammonia gas such as is used in refrigeration. Nitrogen was generated by the reaction of ammonium sulphate and sodium nitrite solutions. Professor J. H. Long kindly suggested an arrangement of the nitrogen generator by which air was excluded from the entire system throughout the work.

Traces of oxygen were removed by pyrogallic acid, while the water vapor was taken out by passage through concentrated sulphuric acid and over phosphorus pentoxide.

Before commencing an exposure a stream of nitrogen was kept flowing through the hood for at least twenty minutes. The same plan was used in filling the hood with ammonia. During an exposure a stream of the gas was kept flowing through the hood, both for the purpose of keeping a fresh supply of the gas about the arc and to drive out the dust which formed.

The spectra of the following four metals have been examined photographically in the region lying between λ 2300 and λ 5300.

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* Astroph. Jour., **12**, 167–175 (1900).

MAGNESIUM.

The ordinary arc lines of magnesium seem to be almost wholly unaffected by substituting nitrogen for air. The heavy spark line at λ 4481, which appears also in the spectrum of the rotating arc, is reduced by nitrogen to about one-fifth its intensity in air. Naturally, the magnesium oxide fluting at λ 5007 is practically blotted out in nitrogen and greatly intensified in oxygen. On the other hand, no new lines make their appearance in nitrogen.

The intensity and reversal of the characteristic line at λ 2852, which are so strongly affected by hydrogen * and ammonia, are unaffected by nitrogen, while the sharp line at λ 4571 is slightly reduced by hydrogen and ammonia, although not changed by nitrogen.

The magnesium-hydrogen fluting beginning at λ 5210, discovered by Liveing and Dewar,† appears in ammonia, as does also the F line of hydrogen. Fairly intense hazy lines at approximately 4580, 4434, 4430, and 4390 also appear in ammonia. These lines are apparently intensified by oxygen also. By nitrogen they are unaffected. A very faint trace of these lines can be seen in air. I have not yet succeeded in identifying them.

TIN.

Of the four metals studied, tin is the one whose spectrum is most modified by changes of atmosphere. In air, nitrogen, and oxygen, the tin arc works well. But in hydrogen and ammonia the arc is very short and is maintained with difficulty.

The intensity of the tin arc in nitrogen is estimated at one-third its intensity in air; while in ammonia its intensity is not more than one-twentieth its intensity in air; and in pure hydrogen it is even less.

Not only is the average intensity of the tin spectrum strongly affected, but also the character and relative intensity of its individual lines. In Kayser and Runge's table of wave-lengths of the tin arc more than forty lines are described as reversed. Many of these reversals show very clearly on my plates. When the arc is surrounded with nitrogen, however, some of these lines appear to be doubly reversed, the rest not reversed at all. On the other hand many of the lines that are reversed in air appear to have their reversal widened by ammonia. These reversals are not affected by an atmosphere of oxygen.

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* Astroph. Jour., **12**, 171 (1900). Liveing and Dewar, Proc. Roy. Soc., **32**, 192.

† Proc. Roy. Soc., **27**, 494–496; **30**, 93–99.

The two very strong spark lines at λ 3351 and λ 3282, appearing also in the spectrum of the rotating arc, have their relative intensity decreased by nitrogen. But by ammonia they are relatively enhanced at least twenty times. In the arc in air, these two lines are barely visible; but in ammonia they become two of the most prominent lines of the spectrum. These two lines are similarly affected by hydrogen The spark line at λ 2368 is also intensified in ammonia but less than the two preceding. The spark lines of wave-lengths 2449, 3471, 3539, 3574, appear plainly in ammonia and hydrogen but not at all in air or nitrogen. They are more enhanced by hydrogen than by ammonia. At λ 3360 and λ 3370 appear two unidentified lines of intensity 6 and 3 (on a scale increasing from 1 to 10), respectively, in ammonia, and not quite so intense in nitrogen, which can scarcely be detected in air and hydrogen. These same lines appear also in the magnesium and zinc arcs in air, nitrogen, and ammonia; but oxygen has the effect of immensely weakening both of them in the tin and magnesium arcs. λ 3370 appears in the tin spark, but λ 3360 does not.

Zinc.

The average intensity of the lines of the zinc arc spectrum is reduced approximately one-half by nitrogen. The width of reversed lines is not affected.

The only zinc lines that suffer a disproportionate reduction by an atmosphere of nitrogen are λ 2558 and λ 2502. These, with λ 5182, are the lines which are enhanced by hydrogen. They are strong spark lines. In ammonia their intensity is two or three times as great as it is in air, although the average intensity of the zinc spectrum is diminished perhaps five times by ammonia.

Iron.

The substitution of nitrogen for air about the iron arc produces very little change in the spectrum. The general intensity is not altered. Compared with the number of lines relatively affected by hydrogen, the number of iron lines affected by nitrogen is small, as has been found to be the case with other metals. Many of the lines that are affected by nitrogen are impurity lines. Of fifty iron lines between λ 3660 and λ 4060 that are markedly enhanced by hydrogen, six are distinctly reduced by nitrogen.

On examination of the region between λ 3600 and λ 4600 I found twenty-six lines that are particularly affected by nitrogen. A few others are slightly changed. Of these twenty-six lines seventeen are from two to ten times as strong in nitrogen as in air. But these seventeen lines were all found to be due to impurities, fifteen belonging to manganese, one to chromium, and one to cobalt. The remaining nine lines are *reduced* by nitrogen to from one-half to one-tenth their intensity in air. Part. if not all, of these lines are iron spark lines.

EFFECT OF EXCLUDING NITROGEN.

The effect of pure nitrogen being so slight, it seemed possible that the presence of so large a percentage of nitrogen in the air about the ordinary arc might account for the smallness of the change. I therefore attempted to determine the effect of nitrogen by a process of exclusion. This was done by substituting for air an atmosphere of commercial oxygen taken from an ordinary stereopticon gas-cylinder. A stream of this oxygen was kept flowing through the hood of the arc.

If the chemical affinity of the electrodes for the atmosphere has any effect on the spectrum, one might certainly expect this effect to be exhibited when such easily oxidizable metals as iron, magnesium, and tin are employed in the atmosphere of oxygen.

Mr. A. S. King* found that the metallic lines were intensified by increasing the supply of oxygen about the *carbon* arc. But just the contrary seems to be true with reference to the *metallic* arc. A current as large as ten amperes was tried with chemically pure magnesium electrodes, but the oxygen had little effect on the working of the arc or the appearance of the so-called "flame." To the eyes the "flame," especially with iron electrodes, appears to be less blue and more yellow.

Of eighteen exposures made with the iron, tin, and magnesium arcs in oxygen, all but one show a greater average intensity for the same length of exposure in air than in oxygen. This is not the only respect in which the action of oxygen on the metallic arc resembles that of hydrogen and ammonia. The metallic lines that have been noted as being relatively enhanced or reduced by hydrogen are precisely the ones which are so affected by oxygen. The changes produced by oxygen are not so great as those produced by hydrogen, but they are in the same direction.

SUMMARY.

The results of these experiments may therefore be summarized as follows:

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* Astroph. Jour., **14**, 329 (1901).

1. The average intensity of the iron and magnesium arcs is not changed by substituting pure nitrogen for air as an atmosphere. The average intensity of the zinc and tin arcs is reduced two or three times by nitrogen. By hydrogen the average intensities are reduced from five to twenty times as much as by nitrogen. Ammonia apparently does not produce quite so great a reduction as does hydrogen.

2. The relative intensity of many lines depends upon the atmosphere. The lines that are relatively reduced by nitrogen are spark lines. As a rule these lines are relatively enhanced by hydrogen or ammonia.

3. The influence of ammonia on intensities and reversals is intermediate between that of nitrogen and hydrogen, and in general it seems true that *the effect of ammonia is approximately equal to the sum of the effects of its constituents.* This, in fact, is the particular point which I had in mind to determine when I began these experiments.

4. *The influence of oxygen is similar to that of hydrogen.*

5. Nitrogen affects the reversed lines of tin by either destroying the reversal or producing faint double reversals.

These results seem sufficient to show that *the readiness of an atmosphere to form chemical union with the electrodes under ordinary conditions is a very small, probably insignificant, factor in determining the intensity of the arc. The intensity appears to be due to electrical causes rather than to chemical reactions.*

Some experiments have been performed by Professor Basquin* which seem to confirm the theory that the intensification of spark lines in hydrogen is caused by the increased resistance due to the hydrogen atmosphere about the arc. This greater resistance has been attributed to the absence of chemical reaction in the hydrogen arc. Such a change of resistance in the products of the arc may explain the phenomena which occur in hydrogen. But if the resistance of the arc depends on the reactions in it this fact makes it difficult to see how the spark lines can be intensified by an atmosphere of oxygen.

This work was done under the direction of Professor Crew, who, in fact, himself began it and to whom I am indebted for continued advice and assistance.

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22 April, 1902.

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* Astroph. Jour., **14**, 14–17 (1901).